Chemical and Process Engineering 2011, 32 (1), 57-68
DOI: 10.2478/v10176-011-0005-7

THE INFLUENCE OF HYGIENISATION OF SEWAGE SLUDGE ON THE PROCESS OF PYROLYSIS

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The aim of this work was to determine the influence of liming on the process of pyrolysis. Three samples of sludge from two wastewater treatment plants were selected for this study on pyrolysis: sludge without liming and limed sludge from the Central Wastewater Treatment Plant in Ostrava and sludge from the Wastewater Treatment Plant in Sviadnov. The samples had different content of calcite ($CaCO_3$). The limed sludge contained 7% of $CaCO_3$, sludge without liming 3.8% and sludge without liming from WWTP Sviadnov contained 0.5% of calcite. The results of laboratory pyrolysis proved that limed sludge released the maximum amount of carbon – 55.46 %, while sludge without liming from WWTP Sviadnov released only 48.92%. Calcite produces during its decomposition CaO and the product influences the pyrolysis process because it supports cracking of volatile organic compounds

Keywords: pyrolysis, sewage sludge, pyrolytic gas, lime

1. INTRODUCTION

Treatment of municipal wastewater produces sludge that contains many contaminants. The content of contaminants substantially influences the treatment of sludge (Raclavská, 2007; Werle and Wilk 2010; Werther and Ogada., 1999). Sludge is processed and reworked by various technological operations such as dewatering, thickening, drying and stabilisation of volume pathogens and smells (Raclavská, 2007; Warman and Termeer, 2005; Werther and Ogada, 1999). Sludge contains organic compounds with a high content of volatile components and can thus be transformed into an exploitable source of energy (Fytili and Zabaniotou, 2008; Hossain et al., 2009; Sánchez et al., 2009). In addition to direct combustion, it is possible to obtain energy from sludge through thermochemical processes such as gasification or pyrolysis. The hygienic safety of sludge must be guaranteed before its thermal utilisation, which is not performed directly by the producer.

Sludge processing by quicklime is the most widely used method for sludge treatment. Hygienisation is achieved through simultaneous effects of a high temperature, alkaline environment and production of ammonium. A usual dose of quicklime is 10 to 20 %, with respect to the dry matter of sludge being treated. Upon addition to the sludge, calcium oxide together with water form $Ca(OH)_2$ (lime slackening). Liming influences the phase composition of sludge. The most conspicuous change is the

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increased content of portlandite, $Ca(OH)_2$, which can be transformed during sludge ageing into calcite, $CaCO_3$ (Raclavská, 2007). The aim of this work is to determine the influence of liming on the process of pyrolysis.

2. PYROLYSIS OF WASTE

Pyrolysis is a process of organic material decomposition in an inert atmosphere at high temperature, forming gaseous, liquid and solid products (Caballero et al., 1997; Conesa et al., 1998; Fonts et al., 2009; Gasco et al., 2007). Research in the field of sludge pyrolysis is focused mainly on the influence of process conditions on the yield of pyrolytical products and their utilisation. The process of pyrolysis can be optimised using process conditions which are dependent on the final utilisation of products (Sánchez et al., 2009). The yield of individual products is influenced mainly by the final temperature achieved and the heating rate (Caballero et al., 1997; Conesa et al., 1998; Fullana et al., 2003; Inguanzo et al., 2002). A high heating rate and final temperature up to 500 °C lead to a more complete thermal decomposition and thus production of a maximum amount of pyrolytic liquid and a minimal amount of pyrolytic coke (Caballero et al., 1997; Conesa et al., 1998; Inguanzo et al., 2002; Sánchez et. al., 2009). Increasing the heating rate results in a faster evaporation of the natural moisture of material into water vapour, which causes gasification reactions and an increase in the amount of gases formed (Domínguez et al., 2006). The influence of the heating rate on the yield of individual fractions is less pronounced at temperatures above 650 °C (Inguanzo et al., 2002). The greatest amount of pyrolytic coke is formed at a low temperature during pyrolysis and with low heating rates (Sánchez et al., 2009). The other factors important in increasing the yield for the products of pyrolysis of organic materials are: the utilised carrier gas (Barbooti et al., 2004), retention time of gaseous products in the pyrolysis chamber (Islam et al., 2008), pressure (Bellais, 2007; Di Blasi et al., 2008; Williams and Slaney, 2007) and the construction of the pyrolysis facility (Arabiourrutia et al., 2007). The yield and properties of pyrolysis products can also be substantially influenced by the presence of catalyst and by the ratio of material/catalyst (Bellais, 2007; Boxiong et al., 2006). Gaseous and liquid products from sludge pyrolysis can be used as sources of energy or as organic substances. Pyrolytic coke can be used as an absorber based on carbon (Caballero et al., 1997; Conesa et al., 1998; Fonts et al., 2009; Gasco et al., 2007; Inguanzo et al., 2002; Menéndez et al., 2004). In addition, pyrolysis could increase the possibility for the concentration of heavy metals into pyrolytic remains, thus avoiding the production of toxic substances formed during combustion (Caballero et al., 1997; Conesa et al., 1998; Domínguez et al., 2006).

The yield of pyrolysis products as well as their composition and properties are also influenced by the content of organic substances and volatile combustible matter (Caballero et al., 1997; Conesa et al., 1998; Fonts et al., 2009; Gasco et al., 2007; Raveendran et al., 1995). Inorganic compounds contained in sludge can influence the process of pyrolysis through their catalytic effects. Some inorganic compounds catalyse decomposition of natural polymers and cracking reactions. In this case, decomposition is faster, and it starts at a lower temperature because the activation energy is lower than that without the presence of inorganic compounds. Larger amounts of pyrolytic coke and gas are formed at the expense of a lower amount of pyrolytic liquid. Additionally, minerals contained in sludge can substantially influence the chemical compositions of pyrolytic liquid and gas (Couhert et al., 2009; Haykiri-Acma et al., 2010; Mészros et al., 2007; Patwardhan et al., 2010; Raveendran et al., 1995). Inorganic components of sludge (CaO, MgO, Al_2O_3) can catalyse the process of releasing gases or influence their composition, thus increasing the H_2 and CO_2 content and decreasing CH_4 and CO content (Liu et al., 2004). Minerals can also catalyse heterogeneous reactions when gases formed through one component of the fuel react with the pyrolytic coke formed from another component (Couhert et al., 2009).

3. METHODS AND MATERIALS

Three samples of sludge from two wastewater treatment plants were selected for this study: sludge without liming (sewage sludge A) and limed sludge (sewage sludge B) from the Central Wastewater Treatment Plant Ostrava (CWWTP Ostrava) as well as sludge from Wastewater Treatment Plant Sviadnov (WWTP Sviadnov), which processes municipal wastewater from the town of Frýdek-Místek (sewage sludge S). Sludge from both wastewater treatment plants were products from the mechanical-biological treatment of wastewater based on the principle of low-load activation with nitrification, preliminary nitrification and dewatering of anaerobically stabilised sludge in centrifuges (CWWTP Ostrava) or in belt presses (WWTP Sviadnov).

The sludge samples were analysed according to the standards CSN ISO 1171, CSN ISO 441375 and CSN P CEN/TS 15104. The content of volatile matter was determined according to the standard CSN ISO 562 (Solid fuels – Determination of volatile matter) in the laboratory of the Mine Karvina, the enterprise Lazy (Co Ostrava-Karvina Mines). The concentration of humic acids contained in the sludge from WWTP was determined according to the method described by Swift (1996). E4/E6 ratios were determined after Chen et al. 1977.

In addition, the samples of sludge were analysed by infrared spectroscopy with Fourier transform (FTIR). Infrared spectra were measured using the Nicolet iS10 spectrometer in the range of 500 to 4000 cm^{-1}.

The phase analysis of the samples was performed using the URD-6/ID 3003 X-ray diffractometer (Rich. Seifert-FPM, Germany) with the following conditions: CoK_{α} X-ray radiation, a 40 kV high voltage, a 35 mA current, a step scan mode with a step of 0.05^{o} 2θ, a 3-s time per step and digital processing of output data. For quantitative analysis, 10 wt % of ZnO was added as an internal standard. The mixture was homogenised by means of micronising milling and measured in a glass cuvette. The manufacturer's software, Rayflex X (RayfleX scanX and RayfleX Analyze, version 2.289), was used for both measurement and data processing. The data evaluation for semi-quantitative analysis was performed using RayfleX Autoquan software, version 2.6, a commercial, modified version of BGMN. The designation of "Autoquan" is indicative to the BGMN program interface for Windows.

Pyrolytic gas was analysed using an Agilent 3000 Micro Gas Chromatograph analyser with a thermal conductivity detector. The following chromatography columns were used: a Plot U (0.32-mm diameter, 3-m length) column combined with a Molsieve (0.32-mm diameter, 10-m length) column and using argon as the carrier gas and a Plot Q (diameter 0.32 mm, length 8 m) column and using helium as the carrier gas. Gases were analysed continually throughout the entire pyrolysis process; the concentrations of hydrogen, carbon dioxide, carbon monoxide and methane were determined at five-minute intervals.

3.1. Composition of sludge

Dry matter in sludge contains from 40 to 60 wt % of organic matter, and the remaining components are inorganic. Sewage sludge consists mainly of bacterial matter (nucleic acids, proteins, carbohydrates and lipids) and their decay products, undigested organic material (cellulose and lignin) and newly produced organic material consisting of humic acids, fulvoacids and inorganic materials. This composition has been reflected in the FTIR spectra of the samples indicative with the occurrence of alcoholic, carboxylic, amide, aliphatic, aromatic and methylene functional groups. The signal for the amide group could come from denatured proteins. Humic acids contain a variety of functional groups, including carboxylic acids (COOHs), phenolic hydroxyl groups (OH), enolic groups (OH), alcoholic groups (OH), quinone, hydroxylquinone and lactone. The infrared absorption bands used for interpretation of functional groups in various kinds of sludge are listed in Table 1. (Filip Z. et al., 1988; Fonts et al.

(2009). The broad bands in the 3600 to 3200 cm^{-1} range are caused by O-H (water, alcohols, phenols and carboxylic acids) and N-H (amines) stretching vibrations (Fig.1).

Table 1. Infrared absorption bands of sewage sludge (Filip Z. et al., 1988)

Absorption band [cm^{-1}]	Occurrence of functional group
3698 - 3620	-OH stretch
3500 – 3400	Primary amides
3350	Secondary amides
3200 - 3000	Aromatics
2980 - 2920	Aliphatic structures, C-H stretching
2300	Stretching frequency, C-N group (Fonts et al., 2009)
1650 - 1550	Amide (CONH)
1519 – 1515	Amide, aromatic ring stretch (C=C)
1600 – 1500	Alkenes and aromatics (C=C)
1463	C-H deformation of CH_2 or CH_3 groups
1425	Aromatic ring stretching
1150 – 1000	Silicates (1080 cm^{-1}); other possible contributions – polysacharides (1150 – 1000 cm^{-1}), aromatics -C-O stretch
913	Cycloaliphatic structures, aromatic structures and phosphorous-phases
535	Si – O – Me in silicates
470	Me-OH in silicates or C-C-C boxing

From the FTIR spectra (Fig. 1), it is apparent that a difference between the sewage sludge S and the sewage sludge samples A and B exists in the first band in the region from 3550 to 3000 cm^{-1}, in which the sewage sludge samples A and B have higher absorption bands for OH groups than sewage sludge S. The absorption bands of the sewage sludge S samples are broader and most likely to coincide with absorption bands of aromatic compounds. Another significant difference between these spectra is in the 1000-cm^{-1} region, which corresponds to silicates.

The difference between the spectra of the sludge processed by liming and the unprocessed sludge is indicated only by the presence of the 2367 cm^{-1} band in the spectrum of the unprocessed sludge as this band corresponds to a C-N group.

The differences in the chemical properties of different kind of sludge were also determined by other methods. The content of humic acids in sludge has a stable value. The content of humic acids, the E4/E6 ratio of absorbances, the HA/FA ratio and the pH value of the studied sludge samples are presented in Table 2. The differences in the ratio of humic acids and fulvoacids (HA/FA) reflect the different content of fulvoacids, which is lower in sewage sludge S. The E4/E6 ratios are determined by

sample absorbances at 465 and 665 nm, respectively. E4/E6 ratios were used to indicate the proportion between aliphatic structure and the degree of aromatic condensation (Gondar et al. 2005). Low E4/E6 ratio corresponds to high aromaticity, which is in accordance with the results for the sewage sludge S.

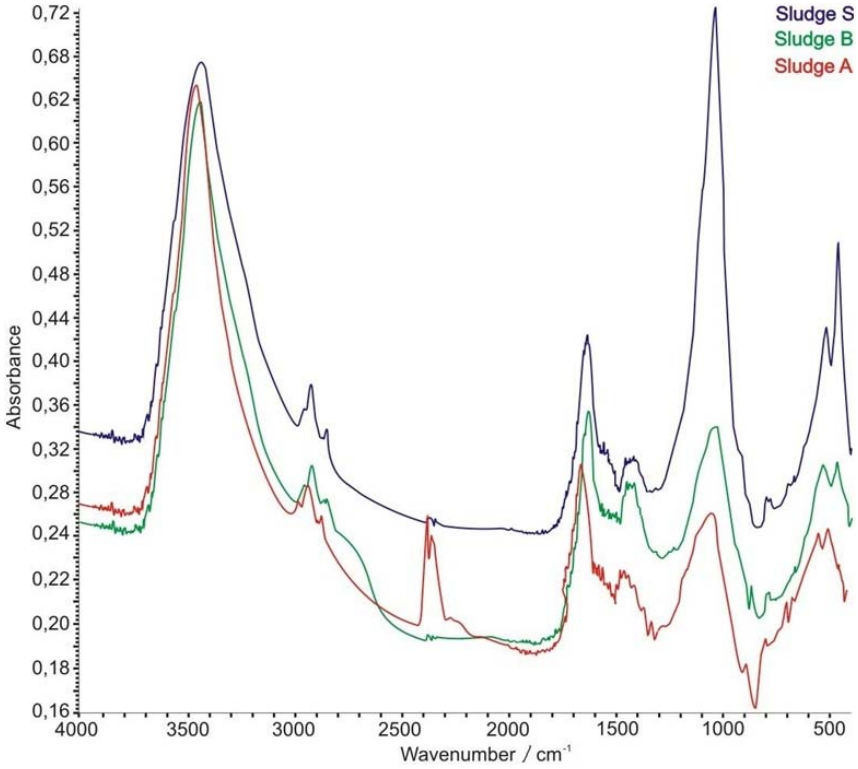

Fig. 1. FTIR spectra of sewage sludge samples A, B and C

Table 2. The parameters characterizing humic matter in different kinds of sludge

	pH	Humic acids [wt %]	E4/E6	HA/FA
Sewage sludge A	8.04	19.47	7.36	1.95
Sewage sludge B	12.24	19.75	5.57	1.94
Sewage sludge S	6.68	19.19	9.58	2.17

X-Ray diffraction was used to determine the most important mineral phases in the studied samples (Table 3). The sewage sludge S contained an increased amount of phyllosilicates (muscovite, chlorite). The sewage sludge samples A and B contained calcite; the sludge processed by liming contained 7 % of calcite compared to 4 % in the unprocessed sludge. A higher content of inorganic matter (ash content) in the sewage sludge S can be seen in Table 4. Proximate and ultimate analyses of the used sewage sludge samples are listed in Table 4.

Table 3. Mineralogical composition of sewage sludge samples (wt % with standard deviation)

		Sewage sludge A	Sewage sludge B	Sewage sludge S
Amorphous		78.09 ± 2.43	74.5 ± 3.3	83.10 ± 2.25
Calcite	$CaCO_3$	3.80 ± 0.78	7.02 ± 1.44	0.58 ± 0.51
Chlorite	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$	1.42 ± 0.72	1.69 ± 0.93	5.02 ± 1.44
Gypsum	$CaSO_4.2H_2O$	0.71 ± 0.45		
Muscovite	$KAl_3Si_3O_{10}(OH,F)_2$	3.10 ± 1.26	2.31 ± 1.38	5.28 ±1.47
Albite	$Na[AlSi_3O_8]$	1.08 ± 0.99		
Quartz	SiO_2	7.67 ± 0.60	7.27 ± 0.60	6.01 ± 0.57
Vivianite	$Fe_3(PO_4)_3 \cdot 8H_2O$	4.45 ± 0.99	7.23 ± 2.16	

Table 4. Proximate and ultimate analyses of the sewage sludge samples

Sample	C	H	N	S	O	Ash	Fixed carbon	Volatile matter	GCV	NCV
	[wt %]								[kJ/kg]	
Sludge A	24.6	3.8	2.9	< 0.1	21.6	50.10	8.4	41.5	8449	7733
Sludge B	22.6	5.1	2.8	< 0.1	19.5	51.20	7.4	41.4	8651	7933
Sludge S	19.3	4.0	2.5	< 0.1	24.2	58.80	11.0	30.2	8564	7999

Explanations: GCV – gross calorific value, NCV – net calorific value

4. LABORATORY PYROLYSIS TESTS

Each sludge sample of 5 kg weight was dried at the temperature of 40 °C until constant weight was reached. The sample was then homogenized, milled in agate mortar of ball mill Pulverisette (manufacturer FRITSCH GmbH) until grain size fraction under 43 μm formed 95%. From the homogenized material, 0.2 g sample was used for pyrolysis tests. Experiments were performed using laboratory pyrolytic equipment manufactured by Parr Co. The main part of this equipment was a Parr Co. steel reactor. Continual heating to 900 °C was provided by a Parr Co. electric heater and temperature controller, type 4836 with a thermocouple of type K. The temperature detector was located in the middle part of the reactor. Pyrolysis was conducted in a nitrogen atmosphere. The flow-meter was located at the entrance of where the inert gas is released into the reactor. The sample was placed between two layers of quartz wool in the middle part of the reactor near the thermocouple. A diagram of the pyrolytic equipment used is shown in Fig. 2. The sludge samples were pyrolysed using the same process conditions to compare the pyrolytic procedures. The flow rate of nitrogen was set at 25 ml per minute. The final temperature of the pyrolytic process was 850 °C, and this temperature was maintained for two hours after reaching this value.

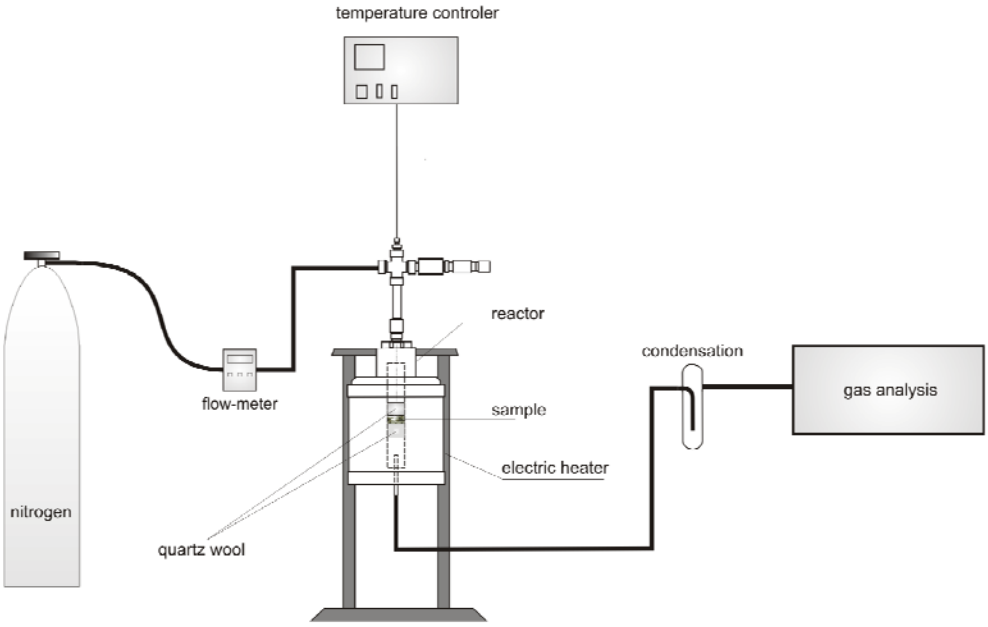

Fig. 2. Diagram of pyrolytic apparatus

5. RESULTS AND DISCUSSION

Table 5 lists the results of the determined major elements in pyrolytic coke. In addition, this table contains the calculated results for the amount of released hydrogen, nitrogen and carbon, which were converted to components of pyrolytic gas. The highest amount of nitrogen was released from the sludge processed by liming, where ammonia was formed and released after an addition of lime. For hydrogen and carbon, there were no substantial differences.

Table 5. Calculation of amounts of released major elements during pyrolysis

Sample	After pyrolysis				Released		
	C	H	N	S	H	N	C
	[%]						
Sewage sludge A	11.661	0.287	0.396	< 0.1	92.36	86.45	54.87
Sewage sludge B	10.074	0.184	0.203	< 0.1	96.37	92.71	55.46
Sewage sludge S	9.857	0.157	0.351	< 0.1	96.10	85.92	48.92

Lin et al. (2009) report that the amounts of carbon, nitrogen and hydrogen in the pyrolytic coke from different kinds of sludge produced by the treatment of wastewater decrease upon increasing the pyrolytic temperature. The strength of bonding in the original material influences the process of desorption. In the progress of pyrolysis, the yield and composition of individual fractions are not always linearly proportional to the content of carbon in pyrolysed sludge, but they can be influenced by different percentages of individual components (humic acids/fulvoacids). The enrichment of pyrolytic coke by carbon increases with the content of fulvoacids in the original sludge (Gascó et al., 2005, Mendéz et al., 2005). The higher number of functional groups in fulvoacids makes this fraction more reactive during pyrolysis, which leads to a higher content of carbon in the pyrolytic coke (Mendéz et al., 2005). The enrichment index for carbon was calculated as a ratio of the content of carbon in

pyrolytic coke to that in sludge, multiplied by 100. The highest value of the enrichment index was for the sludge without treatment by lime, which had an increased content of humic acids with aliphatic structure.

5.1. Influence of hygienisation of sludge on the composition of pyrolytic gases

Gas from the pyrolysis of sludge contains CO_2, CO and H_2 as well as hydrocarbons CH_4, C_2H_4 and C_2H_6 (Werther and Ogada, 1999). The concentration of H_2, CO_2, CO, a CH_4 were determined at intervals of five minutes. The volumes of gases were obtained by calculation using the generally known relationship between the mass and volume of gas. The total volumes of gases released during pyrolysis (related to 1 gram of the initial material) are listed in Table 6.

Table 6. Volumes of measured gases, which were obtained in the pyrolysis process equivalent to one gramme of pyrolysed materials

	H_2	CO	CO_2	CH_4	Total volume of detected gases
	[ml]				
Sewage sludge A	166.4	0	60.7	0	227.1
Sewage sludge B	169.1	19.3	80.3	6.9	275.6
Sewage sludge S	116.3	0	51.9	0	168.2

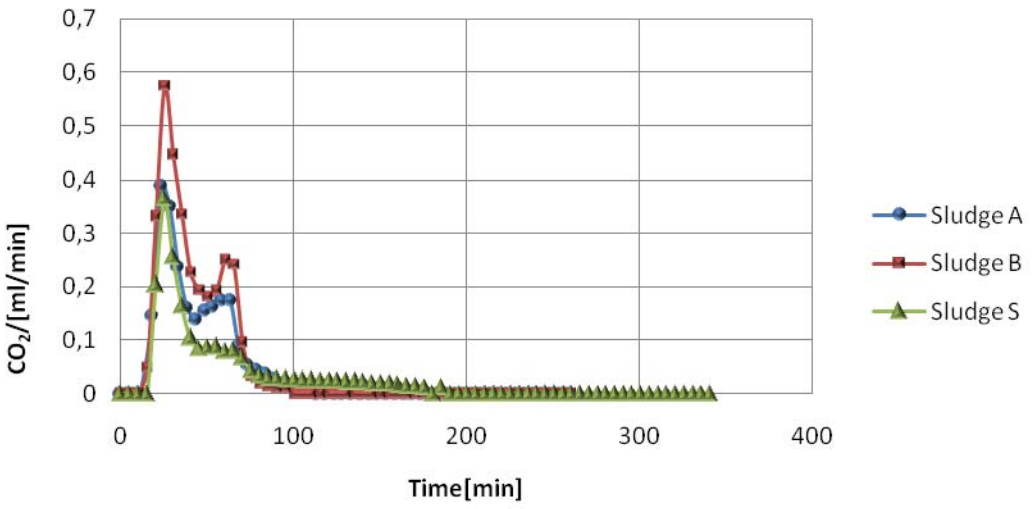

Fig. 3. The progress of carbon dioxide release during pyrolysis

The highest volume of the detected gases was generated through the pyrolysis of limed sludge. The gases released during pyrolysis of sewage sludge A and sewage sludge S had similar compositions. Approximately 70 vol. % of the detected gases were H_2 and 30 vol. % of the detected gases were CO_2. The progress of releasing gases during pyrolysis is illustrated in Figs. 3-5. There was little variation in the progress of limed sludge pyrolysis in which, in addition to hydrogen and carbon dioxide, carbon monoxide (7 vol. % of the detected gases) and methane (2.5 vol. % of detected gases) were formed as well. The limed sludge also has a higher production of carbon dioxide, which is probably caused by the decomposition of the increased calcite content. The highest volume of hydrogen was released from the

limed sludge. The progress of releasing hydrogen from limed sludge is also different in comparison with the two other samples. The progress of releasing gases during the pyrolysis of limed sludge is illustrated in Fig. 5.

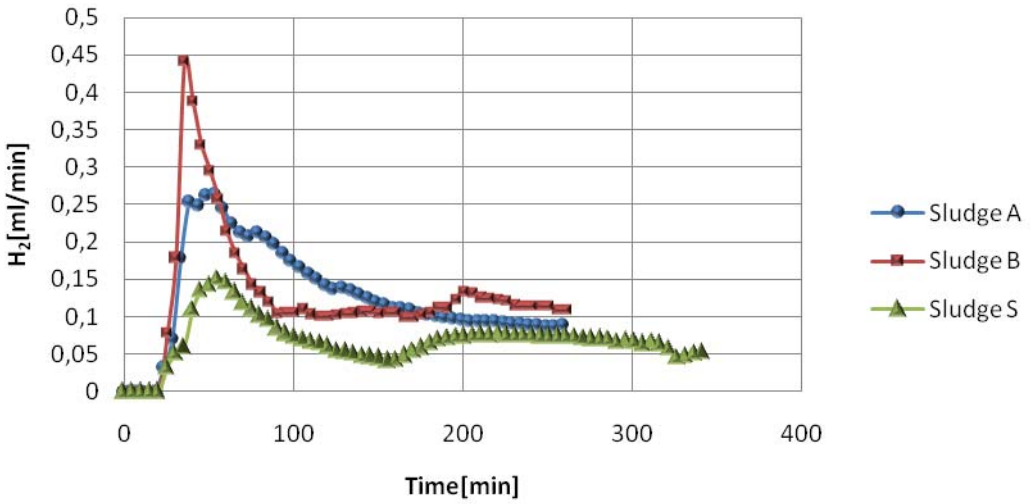

Fig. 4. The progress of hydrogen release during pyrolysis

During the pyrolysis of limed sludge, CO_2, which had two maximums dependent on temperature, was released at the beginning of the reaction. The release of H_2 and CH_4 followed, and then the last component, CO, was released. The decomposition of carbonates occurred at around 65 min., which was identified from the corresponding progress of the release of CO_2 from both the limed sludge and sludge without liming, which contained approximately 4 wt % carbonates. A rapid release of H_2 and CO_2 from the limed sludge is caused by the reaction of CaO with organic compounds containing nitrogen, which is released according to the following equation: proteins → peptides → amino acids → fatty acids + NH_3.

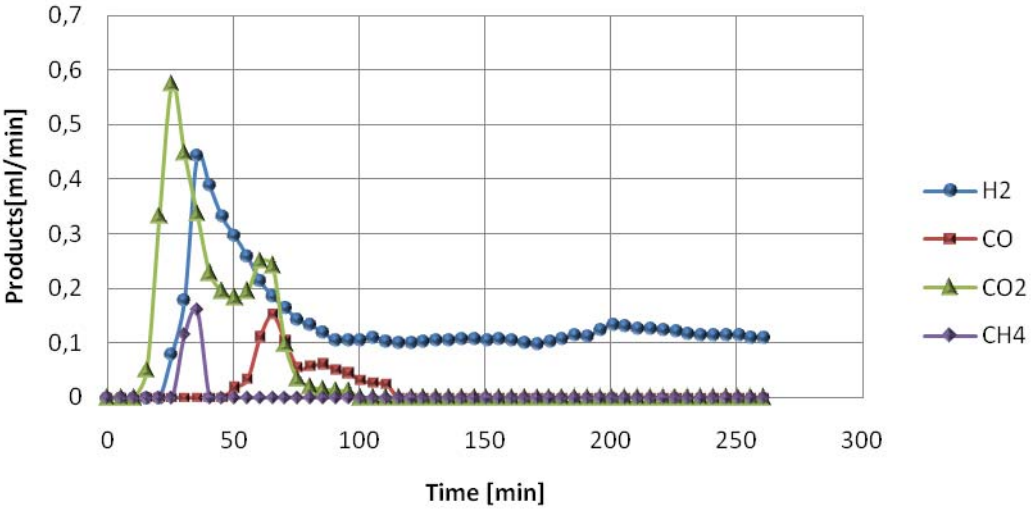

Fig. 5. The progress of gas releasing during pyrolysis of limed sludge B, CWWTP Ostrava

A release of CO is influenced by the Boudouard reaction (1), which requires CO_2 for the production of CO (Menéndez et al., 2004):

$$C + CO_2 \leftrightarrow 2\ CO \qquad (1)$$

The content of CaO in sludge increases its reactivity during pyrolysis; it supports cracking of volatile organic compounds. CaO is active especially in the splitting of oxygen-containing functional groups and the production of carbon dioxide (Liu et al., 2004; Radović et al., 1983). Catalytic reactions initiated by the presence of CaO can also support the release of hydrogen during pyrolysis (Menéndez et al., 2004). If CaO or $Ca(OH)_2$ is present during pyrolysis, it can react and form $CaCO_3$, as shown through Reactions (2) and (3) (Sato et al., 2003). The high content of hydrogen in the pyrolytic gas from the limed sludge can be explained by these reactions.

$$C + CaO + 2H_2O \leftrightarrow CaCO_3 + 2H_2 \quad (2)$$

$$C + Ca(OH)_2 + H_2O \leftrightarrow CaCO_3 + 2H_2 \quad (3)$$

Gaseous products formed by the cracking of volatile compounds in sludge can mutually react. CH_4, CO and CO_2 content can be influenced by continual methanisation, which can be expressed by Equation (4) and (5), according to Menéndez et al. (2004):

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad (4)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad (5)$$

The release of gases during pyrolysis in the sequence of CO_2, H_2, CH_4 and CO indicates that CO_2, which was formed by the decomposition of organic matter and carbonates, participated in the production of methane.

5. CONCLUSIONS

Hygienisation of sludge by lime influences the pyrolytic process. After an addition of CaO, as a result of the decomposition of organic compounds containing nitrogen, the release of H_2 and CO_2 is faster, and it is possible to shorten the retention time in the pyrolytic chamber. As a consequence of a higher amount of CO_2, which originates through the decomposition of carbonates, CH_4 and CO are formed in the pyrolytic process of limed sludge. They can influence the calorific value of the gases from the point of view of their further utilisation.

This work was supported by the research projects MSM 6198910019 (Ministry of Education, Youth and Sport, the Czech Republic) and SV 5410051/2101 - Optimisation of Gas Production during Pyrolysis of Municipal Waste.

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